Electronic supplementary information for

**Aqueous acid-based synthesis of lead-free tin halide perovskites with near-unity photoluminescence quantum efficiency**

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EXPERIMENTAL SECTION

**Chemicals:** n-Octylamine (Aladdin, AR, 99%), Hypophosphorous acid (H₃PO₂, Aladdin, AR, 50 wt. % in H₂O), Hydrobromic acid (HBr, Aladdin, AR, 48 wt. % in H₂O), Hydroiodic acid (HI, Aladdin, AR, 55.0 - 58.0% with ≤1.5 % H₃PO₂), Stannous Oxide (SnO, Aladdin, AR, 99%), Polystyrene (PS, Aladdin) were purchased and used without further purification.

**Synthesis of (OCTAm)₂SnBr₄:** In a typical synthesis, stannous oxide (0.75 mmol) powder was dissolved in 2.5 mL hydrobromic acid by sonication until all SnO powder was dissolved. Then aqueous 15 mL H₃PO₂ was added to avoid the oxidation of the tin, in the meantime, 475 µL n-octylamine was added to the above tin-precursor solution under strong agitation. The solution was heated to 80 °C and maintained for 30 min. The colorless plate-like product with strong yellow fluorescence under UV light was slowly cooled at 4°C. For the synthesis of (OCTAm)₂Sn(Br/I)₄ or (OCTAm)₂SnI₄, the variable compositions were obtained by simply changing the ratios of the halide ions.

**Synthesis of Other (OCTAm)₂SnX₄:** The anion exchange reactions were conducted using (OCTAm)₂SnBr₄ as starting material, while hydroiodic acid was used as iodide source. Specifically, hydroiodic acid was dropwise introduced into the starting solution under strong agitation for a few seconds and the complete anion exchange process was achieved within minutes.

**PS-Perovskite Composite Film Fabrication:** To obtain the film, firstly 25% Polystyrene (PS) dichloromethane solution was mixed with a certain amount of (OCTAm)₂SnBr₄ to get a turbid jelly-like solution. Then, the films were prepared by drop-casting the turbid jelly solution onto a glass slide and let it dried in ambient air.

**White LEDs Lamp Fabrication:** Various weight ratios of yellow (OCTAm)₂SnBr₄, blue (BaMgAl₁₀O₁₇:Eu²⁺) and green (Eu doped silicates, G2762) phosphors were blended well with 25% Polystyrene (PS) dichloromethane solution. The blended phosphors of PS paste were dropped on 365 nm UV LED chip (1W) and dried in air to form white LEDs lamp.
**Characterization Details.** Powder X-ray diffraction (PXRD): PXRD was measured with a Bruker AXS D8 X-ray diffractometer equipped with monochromatized Cu Kα radiation (λ=1.5418 Å). The diffraction pattern was scanned over the angular range of 5-40 degree (2θ) with a step size of 0.03, at room temperature. Transmission electron microscopy (TEM): TEM was performed on an FEI Tecnai G2 F20 electron microscope operating at 200 kV. The available line resolution is about 0.1 nm. Scanning electron microscopy (SEM): SEM was performed on a ZEISS ULTRA55 electron microscope operating at 3.5 kV. Equipped with Energy-dispersive X-ray (EDX) detector. Steady State Photoluminescence Studies: The photoluminescence (PL) spectra were carried out with a Horiba PTI QuantaMaster 400 steady-state fluorescence system or with a homemade fiber fluorimeter system from Thorlabs operating under ambient conditions. Ultraviolet and Visible (UV–vis) Absorption Spectroscopy for Solid Samples: UV–vis spectra were recorded with a Shimadzu UV-3600 plus spectrophotometer equipped with an integrating sphere under ambient conditions. Absolute Photoluminescence Quantum Yields (PLQYs) Measurements for Solid Samples: The absolute fluorescence quantum yields were measured using a Horiba PTI QuantaMaster 400 steady-state fluorescence system with an integrated sphere and double-checked with a Hamamatsu Photonics QuantaTaurus-QY (model: C11347-11) under ambient conditions. Three independent experiments were done and the test errors of the absolute quantum yield values are below 1%. Time-Resolved Photoluminescence Lifetime Measurements for Solid Samples: Time-Resolved PL emission decay curves were collected at room temperature and detected by a Nikon Ni-U Microfluorescence Lifetime System (Confotec MR200, SOL, Belarus) with a 375 nm picosecond laser, and double-checked with a time-correlated single-photon counting system or a Hamamatsu Photonics QuantaTaurus-Tau (model: C11367-11) with 280 nm or 365 nm picosecond lasers under ambient conditions.
**Figure S1.** Additional scanning electron microscopy image of the as-prepared 2D (OCTAm)$_2$SnBr$_4$ perovskites without purification and corresponding EDS spectra of different area in the same sample.

![SEM Image of 2D (OCTAm)$_2$SnBr$_4$ Perovskites](image1)

**Figure S2.** Plots of (ahν)$^2$ vs photon energy (hν) of 2D (OCTAm)$_2$SnBr$_4$ perovskite.

![Plot of (ahν)$^2$ vs Photon Energy](image2)
Figure S3. Time-resolved PL decay and the corresponding fitting curves of the 2D (OCTAm)$_2$SnBr$_4$ perovskites with PL emission at 600 nm and excitation wavelength of 280 nm or 365 nm.

Figure S4. The photographs of products produced with different $\text{H}_3\text{PO}_4$ concentrations (a-c, 50, 25 and 12.5 wt. %) under UV light.
Figure S5. Normalized PL excitation (EX) and emission spectra (PL) of 2D (OCTAm)$_2$SnBr$_4$ PS-perovskite composite film. The inset shows photograph of 2D (OCTAm)$_2$SnBr$_4$ PS film under UV light.

Figure S6. Absolute PL quantum yields spectrum of (OCTAm)$_2$SnBr$_4$ PS-perovskite composite film under different excitation wavelength.
Figure S7. The time-resolved PL decay and fitting curves of (OCTAm)$_2$SnBr$_4$ PS-perovskite composite film with PL emission maximum at 600 nm and excitation wavelength of 375 nm.
Table S1. Comparison of PLQYs values of various halide perovskites synthesized under different conditions.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Structural dimensions</th>
<th>Size</th>
<th>PLQYs</th>
<th>Synthesis conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-(DMEN)PbBr₄</td>
<td>2D</td>
<td>bulk</td>
<td>--</td>
<td>aqueous</td>
<td>S1</td>
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<tr>
<td>(EDBE)PbBr₄</td>
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<td>bulk</td>
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<td>S2</td>
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<tr>
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<td>S3</td>
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<tr>
<td>CsPbBr₂</td>
<td>3D</td>
<td>Micro-crystal</td>
<td>53.9%</td>
<td>aqueous</td>
<td>S4</td>
</tr>
<tr>
<td>(PEA)₂SnI₄</td>
<td>2D</td>
<td>Thin film</td>
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<td>DMF</td>
<td>S5</td>
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<tr>
<td>HMD₃SnBr₈</td>
<td>2D</td>
<td>bulk</td>
<td>86%</td>
<td>DMF/CH₂Cl₂</td>
<td>S6</td>
</tr>
<tr>
<td>(C₄N₂H₁₄X)₄SnX₆</td>
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<td>bulk</td>
<td>near unity</td>
<td>DMF/ CH₂Cl₂</td>
<td>S7</td>
</tr>
<tr>
<td>(C₁₈H₃₅NH₃)₂SnBr₄</td>
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<td>Micro-crystal</td>
<td>88%</td>
<td>octadecene</td>
<td>S8</td>
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<tr>
<td>(OCTAm)₂SnBr₄</td>
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<td>bulk</td>
<td>near unity</td>
<td>aqueous</td>
<td>This work</td>
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References for supplementary information: